BR115041 (2)

Tech Memo M&S 1155

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AD-A229 046

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Technical Memorandum

August 1990

Molten Salt Electrolytes in High Temperature Batteries

by

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Technical Memorandum Mat/Str 1155

Received for printing 1 August 1990

MOLTEN SALT ELECTROLYTES IN HIGH TEMPERATURE BATTERIES

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SUMMARY

This Paper describes the use of molten salt electrolytes in high temperature batteries, both single-use 'thermal' batteries and high temperature rechargeable batteries. The properties of the existing electrolytes are discussed and current research on new electrolytes is described. Keywords: Great Britain. (RH)

Text and Vu-graphs of a lecture given by A.G. Ritchie to the Molten Salts Discussion Group of the Royal Society of Chemistry at their Summer Meeting, 4-6 July 1990, University College of Swansea.

The Vu-graphs are attached with the discussion which is numbered to correspond with the Vu-graphs.

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LIST OF CONTENTS

2 HIGH TEMPERATURE BATTERIES USING MOLTEN SALT ELECTROLYTES

There are two main types of batteries which use molten salt electrolytes: thermal batteries and high temperature rechargeable batteries. In both cases, the advantages of molten salt electrolytes are their high conductivity which leads to very high power density (in the thermal batteries > $1A/cm^2$ can be passed) or to high energy density in the rechargeable batteries (in comparison with the alternative ambient temperature lead-acid batteries). The high power density and the very long storage life without maintenance of the thermal batteries makes them ideally suited to providing electrical power supplies for missiles. However their high cost and limited energy density (due to the heavy weight of the steel case and the weight of the pyrotechnic and insulators) precludes them from other applications. The high temperature rechargeable batteries are being developed for submarine propulsion (ARE, Holton Heath) and for electric vehicles (Argonne National Laboratory, USA).

3 CHEMISTRY OF HIGH TEMPERATURE BATTERIES

Almost all modern batteries use lithium as the anode because of its high electrode potential, its high Coulombic capacity due to its low atomic weight and its reasonable chemical stability which allows it to be handled in dry rooms, rather than inert atmosphere glove boxes. Two electrolytes have become established for use in high temperature batteries: the lithium chloride-potassium chloride binary eutectic (melting point 352°C) and the lithium fluoride-lithium chloride-lithium bromide ternary eutectic (melting point 445°C). Binary eutectic has the advantage of the lower melting point but, in practice, high currents cannot be passed at temperatures only slightly above the melting point due to lithium concentration changes on passing current raising the melting point. A further disadvantage is that potassium-containing phases (J-phase $LiK_6Fe_{24}S_{26}Cl$) may precipitate in contact with iron sulphide (formed by discharge of iron disulphide cathode material). Iron disulphide is the present cathode material as it has an adequate voltage, a good conductivity, a high Coulombic capacity (low equivalent weight) and is stable in contact with molten salt electrolytes. However a higher voltage would be desirable and iron disulphide has only limited thermal stability.

4 A LITHIUM ANODE THERMAL BATTERY

This diagram shows a cut-away of a typical thermal battery. The anode, cathode, electrolyte and pyrotechnic pellets are clearly displayed and the insulation, case and terminals, which add significantly to the battery size and weight are shown. The battery is activated by applying a current pulse to the igniter terminals which fires the igniter, ignites the side ignition strip which ignites the pyrotechnic pellets which burn, heating the battery and melting the electrolyte. Once the electrolyte is molten, current can flow and the battery can provide energy.

5 LAIS - POWER SOURCE FOR THE 1990s

LAIS is Lithium Aluminium Iron Sulphide, the high temperature rechargeable battery using lithium-aluminium alloy anode with iron sulphide cathode which is being developed at the Admiralty Research Establishment at Holton Heath by Dr J B Jones and his group for submarine propulsion. The great advantage of the LAIS battery over the existing lead-acid battery is its smaller size and weight and higher power capability. It is also more efficient in the use of fuel.

6 LITHIUM ALUMINIUM/IRON SULPHIDE (LAIS)

This Vu-Graph shows the chemistry of the charging and discharging reactions of this battery, illustrates the processing of materials, the formation of components and illustrates the final battery module. The charge/discharge cycle shows the high efficiency of the battery (virtually 100% charge efficiency, over 85% energy efficiency).

7 ADVANTAGES OF MOLTEN SALT ELECTROLYTES

The advantages of molten salts as battery electrolytes are that they have high conductivity so high currents can be drawn and high power densities obtained, they are thermally stable, have good chemical stability towards anodes and cathodes and they are cheap and readily available. Their disadvantages are their high melting points which necessitate high heat inputs to activate batteries and may cause thermal management problems. A further disadvantage is that they are often hygroscopic and so must be handled in dry rooms.

8 SPECIFICATION FOR THERMAL BATTERY ELECTROLYTES

They need to be good conductors of lithium ions (for batteries with lithium-based anodes) at the operating temperatures of the batteries (typically 350-600°C, the lower limit being set by the electrolyte melting point and the upper limit being determined by melting of lithium alloy anodes or the thermal decomposition of the iron disulphide cathode). Thermal batteries may be used in tropical climates and storage temperatures up to 70°C are possible so no electrolyte conductivity at that temperature is permitted, otherwise the battery would discharge. No electronic conductivity of the electrolyte is allowed either during storage or operation of the battery to avoid short-circuits. The electrolyte (and other battery components) must retain their shape during storage and operation as they are hermetically sealed in a steel can and they must retain their positions. The electrolyte should be chemically stable (at least kinetically and preferably thermodynamically) to both anode and cathode and should also be thermally stable at battery operating temperatures.

9 RESEARCH ON NEW ELECTROLYTES FOR THERMAL BATTERIES

The main aim is to develop lower melting electrolytes to reduce battery case temperatures (because a thermal battery may be in close contact with electronic components in a missile), to reduce the quantity of pyrotechnic needed to heat the battery to its operating temperature and so reduce battery size and weight and to delay electrolyte freezing, thus prolonging the life of some designs of battery.

A further aim is to develop oxidation - resistant electrolytes to allow higher voltage cathodes to be used.

10 RECENT DEVELOPMENTS IN ELECTROLYTES

There has been considerable interest in a lower melting ternary electrolyte for thermal batteries using the lithium chloride-lithium bromide-potassium bromide eutectic, melting point 325°C. This has the advantage of a lower melting point but, more particularly, it can pass worthwhile currents at temperature much closer to its melting point than binary electrolyte (lithium chloride-potassium chloride), probably due to its higher lithium content. It has also proved to be beneficial in high temperature rechargeable batteries as the reduction in operating temperature reduces decomposition of the iron disulphide cathode and so extends the life of the battery.

Nitrate electrolytes are being investigated as low temperature electrolytes with melting points far below those of the halide mixtures currently used. They have the additional advantages of stability to highly oxidising cathodes so higher cell voltages can be obtained. However, they are not thermodynamically stable to lithium-containing anodes and, at high temperatures, fires have resulted, so care is necessary in their use.

11 ALTERNATIVES TO MOLTEN SALT ELECTROLYTES

Possible alternatives to molten salt electrolytes are solid electrolytes and conducting glasses. Many lithium salts conduct lithium ions to some extent at high temperatures and lithium sulphate is a very good ionic conductor above 575°C. However this temperature is too high for practical thermal batteries, as it is close to the melting point of lithium-aluminium alloy anodes and the decomposition temperature of cathode materials such as iron disulphide. Lithium sulphate can be used to demonstrate the principle of solid lithium-conducting electrolytes for thermal batteries. Lithium-conducting glasses are another possibility.

12 CONCLUSIONS

Molten salts electrolytes are already used in thermal batteries and are the electrolytes in high temperature rechargeable batteries which are at an advanced state of development. Electrolytes are being actively researched for high temperature batteries both to reduce the operating temperature and to extend the potential range of the cathode materials used.

Fig 1

MOLTEN SALT ELECTROLYTES IN HIGH TEMPERATURE BATTERIES

A G RITCHIE

MATERIALS AND STRUCTURES DEPARTMENT
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Fig 2

HIGH TEMPERATURE BATTERIES USING MOLTEN SALT ELECTROLYTES

- "THERMAL" BATTERIES
  - SINGLE USE RESERVE BATTERIES (USED IN MISSILES)
    (RESEARCH AT RAE, FARNBOROUGH)

- RECHARGEABLE BATTERIES
  - FOR SUBMARINE PROPULSION
    (RESEARCH AT ARE, HOLTEN HEATH)

CHEMISTRY OF HIGH TEMPERATURE BATTERIES

ANODE - LITHIUM (OR LITHIUM ALLOYS)

ELECTROLYTE - BINARY (LiCl-KCl MPt 352°C)

OR TERNARY (LiCl-LiF-LiBr MPt 445°)

CATHODE - IRON DISULPHIDE FeS_2

(OR SOMETIMES IRON SULPHIDE FeS IN RECHARGEABLE BATTERIES)

Fig 4

A LITHIUM ANODE THERMAL BATTERY

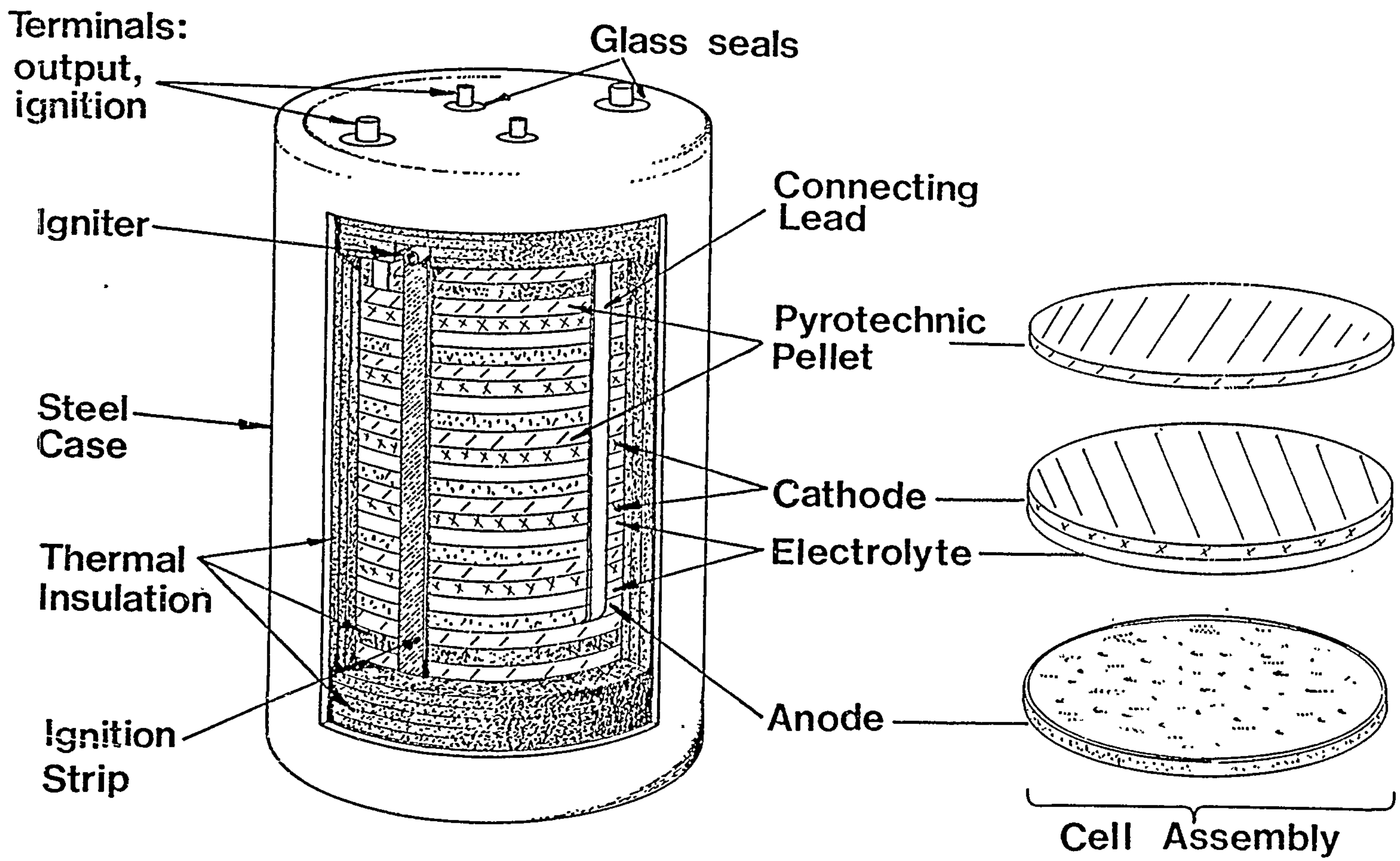

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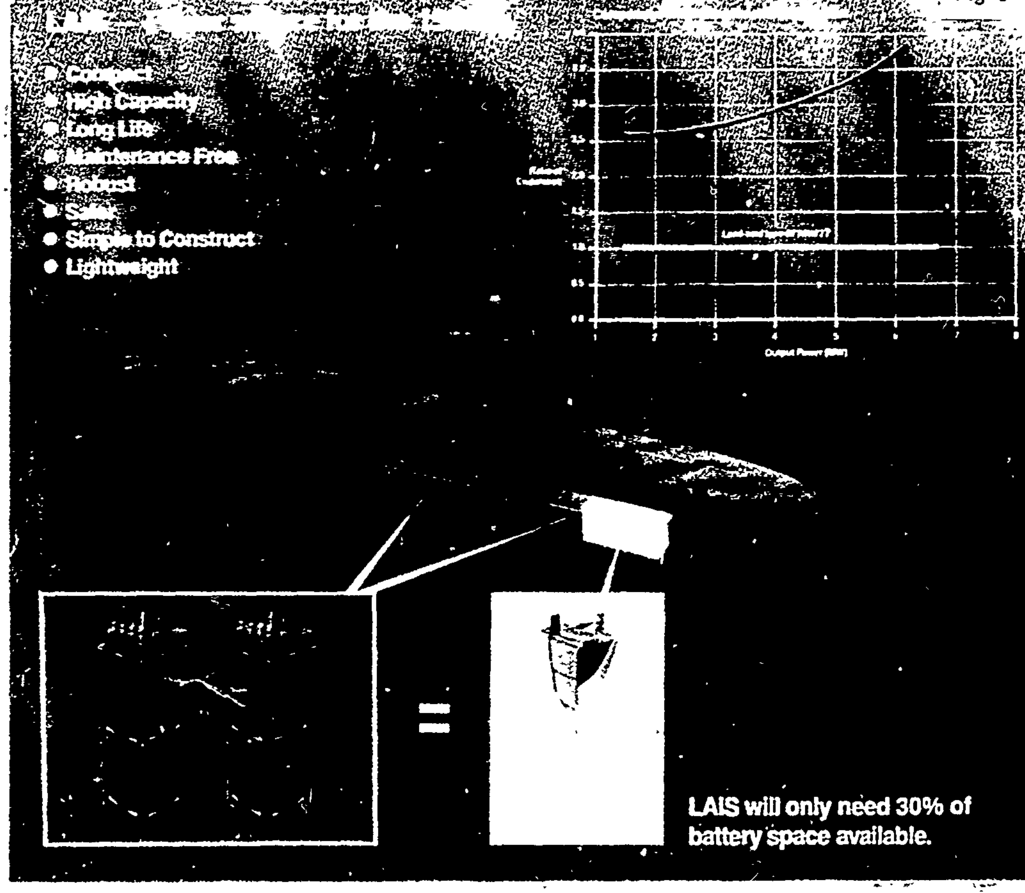
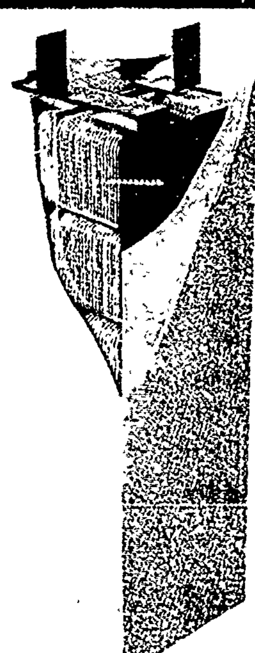
Fig 5





The LAIS high temperature rechargeable battery

The LAIS battery will operate satisfactorily over a wide temperature range typically, from 350°C to 550°C, when the electrolyte is molten.

A model of a full scale submarine sized battery is shown below. This battery has a capacity of 45kWh and an on-load voltage of 24V. The energy density of this LAIS battery is three times greater than the present Lead Acid battery.

Fig 6

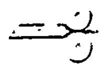
Lithium Aluminium/Iron Sulphide (LAIS)

Anode	Separator	Cathode
Li(Al) /	LiF, LiCl, LiBr, KX, MgO /	FeS

$$2Li(Al) + FeS \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_2S + Fe + 2(Al)$$

E = 1.35 volt

Preparation of Materials

Grinding 

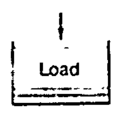
Drying 

Mixing 

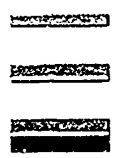
Sintering 

Cell Components Production

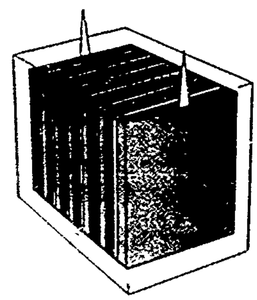
Cold or Hot Pressing



Single or Multicomponent Pressing

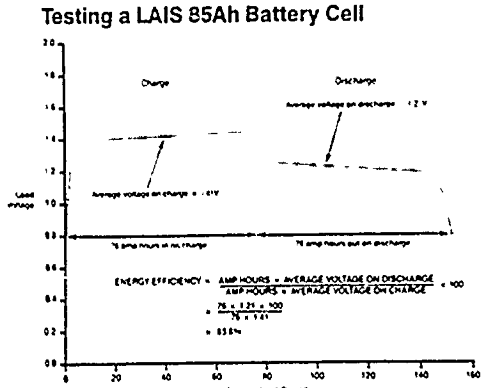


Battery Module Produced



Sub-Unit
(6 Cells)

Testing a LAIS 85Ah Battery Cell



THEORETICAL BATTERY CAPACITY = AMPERE HOURS OF ACTIVE MATERIAL IN ELECTRODE

LITHIUM UTILISATION = $\frac{\text{AMP HOURS OF DISCHARGE}}{\text{THEORETICAL CAPACITY (Ah)}} \times 100$

= (76/85) × 100%

= 89.4%

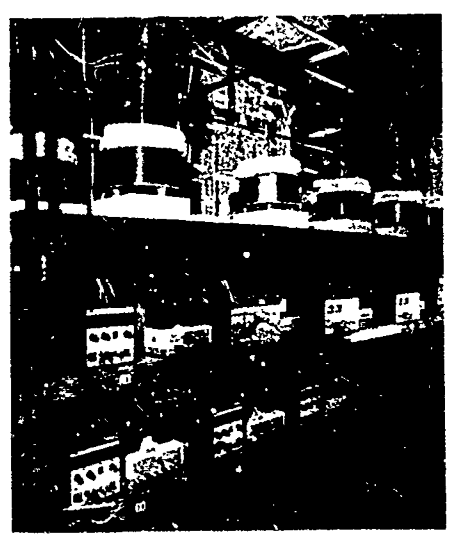


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Fig 7

ADVANTAGES OF MOLTEN SALT ELECTROLYTES

- HIGH CONDUCTIVITY, SO HIGH CURRENT AND POWER
- THERMAL STABILITY
- CHEMICAL STABILITY TO ANODES AND CATHODES
- CHEAP, READILY AVAILABLE

DISADVANTAGES

- HIGH MELTING POINTS
- OFTEN HYGROSCOPIC

Fig 8

SPECIFICATION FOR THERMAL BATTERY ELECTROLYTES

- GOOD LITHIUM ION CONDUCTIVITY AT BATTERY OPERATING TEMPERATURES (350 - 600°C)
- NO LITHIUM ION CONDUCTIVITY AT BATTERY STORAGE TEMPERATURES (UP TO 70°C)
- NO ELECTRONIC CONDUCTIVITY
- DIMENSIONAL STABILITY DURING STORAGE AND OPERATION
- CHEMICAL STABILITY TO LITHIUM AND CATHODE MATERIALS
- THERMAL STABILITY TO 600°C

Fig 9

RESEARCH ON NEW ELECTROLYTES FOR THERMAL BATTERIES

- AIM TO DEVELOP LOWER MELTING ELECTROLYTES
  - TO REDUCE BATTERY CASE TEMPERATURES
  - TO REDUCE AMOUNT OF PYROTECHNIC HEAT SOURCE
  - TO DELAY ELECTROLYTE FREEZING
- AIM TO DEVELOP OXIDATION RESISTANT ELECTROLYTES
  - TO ALLOW HIGHER VOLTAGE CATHODES TO BE USED

Fig 10

RECENT DEVELOPMENTS IN ELECTROLYTES

- NEW LOWER MELTING TERNARY ELECTROLYTE (LiCl-LiBr-KBr) MPt 325°C
  - EXPECTED ADVANTAGES FOUND IN THERMAL BATTERY CELL TESTS
  - ALSO BENEFICIAL IN Li(Al)/FeS_2 RECHARGEABLE BATTERIES

- NITRATE ELECTROLYTES
  - MUCH LOWER MELTING (EG LiCl-$LiNO_3$-$NaNO_2$ 150°C)
  - HIGHER VOLTAGE CATHODES POSSIBLE (EG $Ag_2 CrO_4$)
  - DANGER OF FIRES AT HIGH TEMPERATURE (350°C)

Fig 11

ALTERNATIVES TO MOLTEN SALT ELECTROLYTES

- SOLID ELECTROLYTES (EG Li_2SO_4-BASED, ABOVE 500°C)

- CONDUCTING GLASSES

Fig 12

CONCLUSIONS

- MOLTEN SALT ELECTROLYTES ALREADY USED IN THERMAL BATTERIES

- RECHARGEABLE MOLTEN SALT ELECTROLYTE BATTERIES AT AN ADVANCED STATE OF DEVELOPMENT

- FURTHER RESEARCH NEEDED ON MOLTEN SALT, SOLID AND GLASS ELECTROLYTES TO REDUCE OPERATING TEMPERATURES AND TO EXTEND POTENTIAL RANGE

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Overall security classification of this page

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1. DRIC Reference (to be added by DRIC)	2. Originator's Reference	3. Agency Reference	4. Report Security Classification/Marking
	RAE TM MS 1155		UNLIMITED

5. DRIC Code for Originator	6. Originator (Corporate Author) Name and Location
7673000W	Royal Aerospace Establishment, Farnborough, Hants, UK
5a. Sponsoring Agency's Code	6a. Sponsoring Agency (Contract Authority) Name and Location

7. Title Molten salt electrolytes in high temperature batteries

7a. (For Translations) Title in Foreign Language

7b. (For Conference Papers) Title, Place and Date of Conference

8. Author 1. Surname, Initials	9a. Author 2	9b. Authors 3, 4	10. Date	Pages	Refs.
Ritchie, A.G.			August 1990	17	-

11. Contract Number	12. Period	13. Project	14. Other Reference Nos.

15. Distribution statement
(a) Controlled by –
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16. Descriptors (Keywords) (Descriptors marked * are selected from TEST)

Battery. Missile. Submarine.

17. Abstract

This Paper describes the use of molten salt electrolytes in high temperature batteries, both single-use 'thermal' batteries and high temperature rechargeable batteries. The properties of the existing electrolytes are discussed and current research on new electrolytes is described.

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